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The Structure of Water Monolayers on a Hydroxylated Chromium Oxide Surface

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Abstract. We have investigated the structure of monolayer water molecules on a hydroxylated (001) plane of Cr_2O_3 using GCMC simulations. The water molecules are adsorbed commensurately in the center of three surface hydroxyl groups by directing the proton of a water hydroxyl group towards the solid surface. Another type of water is adsorbed by bridging anchored water molecules, whereby, a two-dimensional (2D) condensed layer is formed. It was ascertained that 2D condensed monolayer water is not in a crystalline state below the 2D critical temperature (319 K), but is composed of many hexagonally linked rings. Above the 2D critical temperature, the hexagonal alignment of water changes to form a one-dimensional linked water structure.

Keywords: adsorption, chromium oxide, 2D water, supercritical water, GCMC

1. Introduction

Metal oxides are one of the most common substances found in nature, and are present in various forms, e.g., minerals, rusts, and synthesized industrial materials, and in general, metal oxides are in contact with either liquid or atmospheric water. Thus, the interfacial properties of metal oxide–water systems play an important role in many physico-chemical processes, and have been studied for many years from various viewpoints. It is known that metal oxide surfaces become hydrated with water molecules to form hydroxylated surfaces (Zaki et al., 1987; Knözinger et al., 1980; Zecchina et al., 1971). Surface hydroxyl groups are essential for the adsorption of water molecules, and are believed to form hydrogen bonds during the adsorption process. In other words, when adsorption occurs, water molecules register with the surface hydroxyl groups. The adsorption isotherms of many metal oxide surfaces are usually either Type II or Type III, as defined by Brunauer et al., BDDT (Micale et al., 1976; Morimoto et al., 1980; Brunauer et al., 1940). However, in 1968, Morimoto et al. found a clear stepwise adsorption isotherm of water on a hydroxylated ZnO surface (Morimoto et al., 1968). This type of adsorption isotherm is also observed in inert gas (Lennard-Jones (LJ) gases)–graphite surface systems (Thomy et al., 1972). This indicates that the interaction of water molecules with a solid surface is not so strong, and the lateral interaction of adsorbed water molecules plays an important part in adsorption. We have found various other oxide systems exhibiting such isotherms, e.g., SnO_2, Cr_2O_3, $HCrO_2$, and BeO (Morishige et al., 1981; Kittaka et al., 1984; Miyazaki et al., 1985).

Among these above, water molecules on a Cr_2O_3 surface form an exceptionally well-defined two-dimensional (2D) phase (Fig. 1). The 2D critical temperature was determined to be $T = 303$ K from precise measurements of the adsorption isotherms at various temperatures, i.e., the transition from gas phase–condensed phase equilibrium to supercritical phase was observable. This has led us to study the molecular processes and structures in detail.

The dynamic properties of a water monolayer on a Cr_2O_3 surface have been studied using quasi-elastic neutron scattering (QENS) and dielectric

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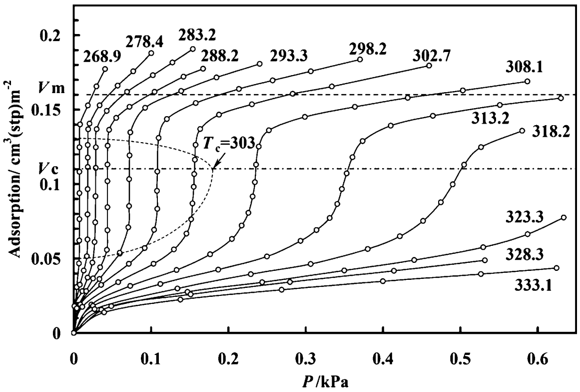

Figure 1. Experimental adsorption isotherms of water on the hydroxylated Cr_2O_3 surface.

measurements (Kuroda et al., 1999). Rotational motion is observed below the 2D critical temperature, and this is discontinuously accelerated in the super critical temperature range. The characteristic crystal plane for this phenomenon was determined to be the (001) plane among some kinds of possible planes. The change in vibrational properties of the adsorbed water was examined using FT-IR measurements (Kittaka et al., 1992). The two typical sharp IR stretch bands associated with surface hydroxyl groups (ca. 3656 and 3408 cm^{-1}) were assigned to the hydroxylated (001) plane. The adsorption of water on the (001) surface displaced the two IR stretch bands to 3618 and 3336 cm^{-1}, respectively, without loosing any sharpness. These two bands become broader above the 2D critical temperature of water, in parallel with further broadening from physisorbed water. This suggests that the phase properties of physisorbed water affect the spectral properties of the substrate.

In this paper, we propose a structure of monolayer water spread over a hydroxylated (001) plane on Cr_2O_3 from Grand Canonical Monte Carlo (GCMC) simulations assuming a simple hydroxylated structure.

2. GCMC Simulations

A hydroxylated Cr_2O_3surface was constructed using 6 × 6 unit cells arranged along the a- and b-axis directions (by 29.72 Å for each) to form a rhombic sheet with a thickness of one unit cell along the c-axis direction. The (001) planes of the solid were thus exposed for the adsorption of water. This solid was put into a working space with a height = 50 Å and a rhombic base. The (001) plane of cleaved Cr_2O_3 is polar, and thus, was prepared arbitrarily so that an electrically neutral surface was exposed. Surface hydroxyl groups were formed by placing dissociated water molecules on this surface, whereby the surface hydroxyl groups were arranged in a planar hexagonal arrangement with their protons protruding normal from the surface. The ionic charges of the atoms in the system were as follows: H (H_2O) = +0.417; H (surface hydroxyl groups) = +0.400; O (H_2O) = 0.834; O (surface hydroxyl groups) = −0.800; and Cr = +1.200. The ionic charges on the water molecule were taken from the TIP3P model, and the ionic charges of the surface hydroxyl groups were arbitrarily selected from the former, allowing for charge balance. The cut-off length for the dispersion force was 15 Å. The software program used was "Sorption," operated by the Cerius2 v4.2 package, using an O2 SGI workstation. The dispersion force was calculated using a universal field. The simulation was mainly done for adsorption branch. Desorption branch coincided with the former at higher temperatures above 353.1 K, below which it took much time and was omitted.

3. Results and Discussion

3.1. Adsorption Isotherm

Figure 2 shows the adsorption isotherms of water on a hydroxylated Cr_2O_3 surface, as determined by GCMC calculations. Under the conditions used, it was not possible to obtain an absolute phase diagram that is comparable with an experimental phase diagram (Morishige et al., 1981). However, a qualitative analysis was successfully conducted. The isotherms are typical of the adsorption of molecules on a homogeneous solid surface with lateral interactions, and exhibit a vertical increase, indicating the coexistence of dense and less dense phases below a critical point. Monolayer coverage was determined by the Point b method at about 0.36 cm^3 (STP) m^{-2}. This is very close to the 0.36 cm^3 (STP) m^{-2}calculated from the molecular area. As was carried out for the experimental data, the slope of [d$\ln P$/dV_{ad}] at the inflection points was plotted versus temperature (not shown). This slope should be zero in the region where the two phases coexist below the 2D critical temperature, and increase at temperatures above the 2D critical temperature. The 2D critical temperature was determined to be at T = 317 K from the crossover point on the abscissa. This value is close to the experimental 2D critical temperature of 303 K.

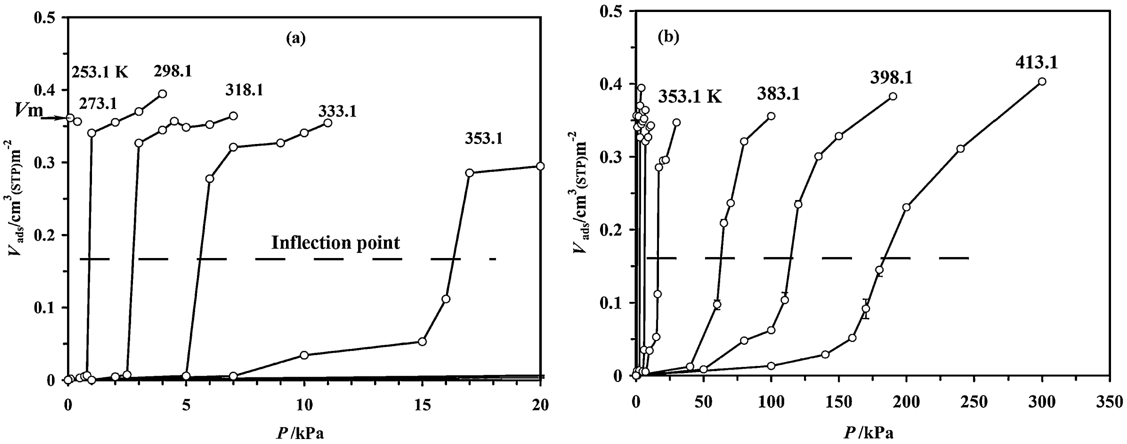

Figure 2. The adsorption isotherms of water on a hydroxylated Cr_2O_3 surface simulated using GCMC.

3.2. Structure of the Adsorbed Water Molecules

Snapshots of the monolayer structures of adsorbed water molecules are shown in Fig. 3. In our GCMC simulations, the structure of the adsorbed layer (density) fluctuated, even under equilibrated conditions. Accordingly the selected examples are shown as a function of temperature. It was found that the structure of water molecules adsorbed at lower temperatures ($T = 253.1$ K) was a partially decomposed 2D hexagonal network of water (i.e., the (001) plane of hexagonal ice I). The water molecule marked with "*" in Fig. 3(a), anchored its proton at a special site, which is at the center of three surface hydroxyl groups, and is present in the hexagonal solid structure. At low temperatures, all of these sites are occupied by water molecules. This

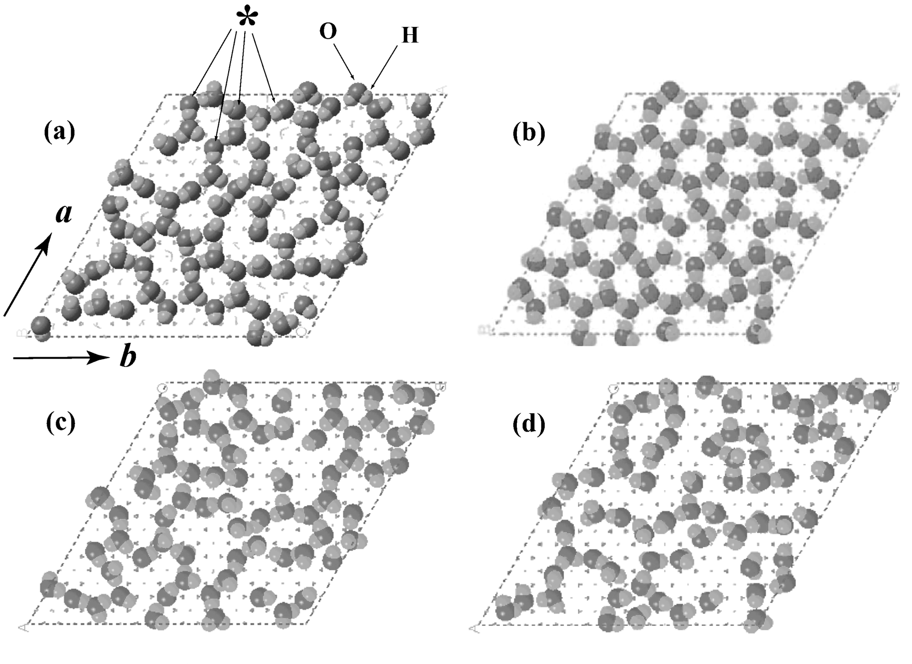

Figure 3. Snapshots of the structure of monolayer water adsorbed on a hydroxylated Cr_2O_3 surface simulated using GCMC. Conditions: (a) $T = 253.1$ K, $P = 0.09$ kPa; (b) $T = 273.1$ K, $P = 0.4$ kPa; (c) $T = 333.1$ K, $P = 11.0$ kPa; and (d) $T = 413.1$ K, $P = 240$ kPa.

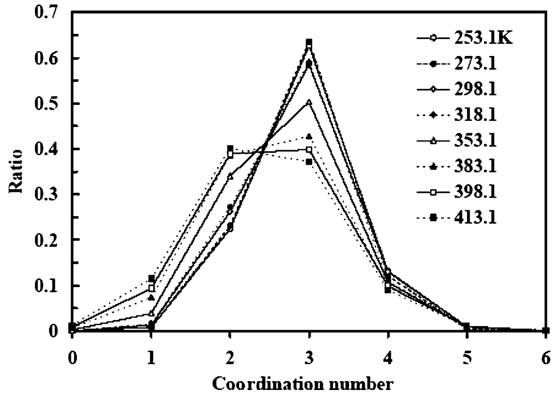

Figure 4. Distribution of coordination numbers of monolayer water molecules on a hydroxylated Cr_2O_3 surface.

orientation of the water molecules is different from the concept where water molecules are adsorbed via hydrogen bonds with the surface hydroxyl groups (Kittaka et al., 1984). Verification for this orientation is now underway using FT-IR measurements and modeling analysis. One supporting factor for this structure is the fact that the displacement of stretching band upon adsorption of water is clear, without any loss of sharpness, i.e., hydrogen bonds are not involved in the adsorption, as in general, the -OH group stretching vibration is broadened by hydrogen bonding, which is not observed in this system (Kittaka et al., 1992).

Other water molecules are adsorbed by forming bridges via hydrogen bonds with the anchored water molecules described above, in which a number of hexagonal rings of water are formed (by chance fully ordered at $T = 273.1$ K in Fig. 2(b). The bridges leading to the formation of the 2D phase of water molecules are reflected in the stepwise adsorption isotherms. With increasing temperature, the bridging of the water molecules becomes broken, and the hexagonal ring structures loosen, which becomes evident above the 2D critical temperature. Here, it is noteworthy that additional water molecules are all adsorbed with the anchored waters as a laterally connected assembly, or at least, as strings. This suggests that the adsorption of water on a hydroxylated Cr_2O_3 surface only occurs when lateral interaction is possible.

Figure 4 shows the coordination number of monolayer water molecules within a distance of 3.5 Å. This was estimated from a number of snapshots (ca. 200–500) taken at equilibrium, showing the derived coordination numbers plotted in the range 0–6. The near zero number for a coordination number = 0 indicates that water molecules are not adsorbed as 2D gas molecules on the surface, even at low temperatures. That is, water molecules are not adsorbed singly, but are absorbed along with an accompanying molecule. This was similar in the lower pressure ranges. On formation of the hexagonal net of water molecules, the coordination number = 3. This condition is depicted by the most common coordination number for the low temperature system.

However, the presence of some water molecules with coordination numbers of 2 and 4, even at a temperature of $T = 253.1$ K, suggests that the hexagonal structure does not completely exist throughout the surface. It is interesting to note here, that for 318.1–353.1 K, there is a marked change in coordination number from 3 to 2 and 1. That is, marked structural changes have had to occur over this temperature range. Above this

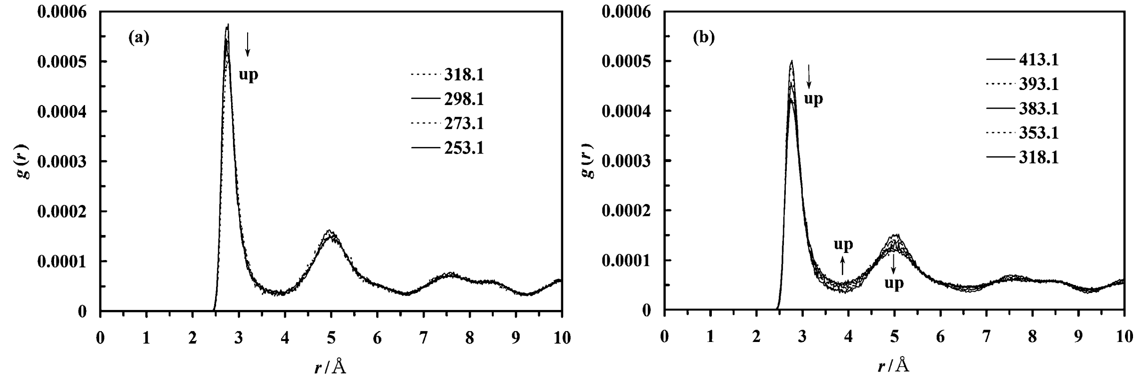

Figure 5. Changes in the radial distribution function of monolayer water (from the water oxygen atoms) on a hydroxylated Cr_2O_3 surface with changes in temperature.

temperature range, the coordination number becomes more non-specific. This transition is directly be related to the 2D critical temperature of $T = 319$ K, determined from the adsorption isotherms.

Furthermore, Fig. 5 shows the radial distribution function of the oxygen atoms of water in the monolayer. Up to $T = 318.1$ K, the radial distribution curves are similar. As the temperature increases, the distribution curves become diffuse, and three peaks (at 2.77, 5.01, and 7.67 Å) decrease in height, accompanied by a shallowing of the peak saddles. That is, above the 2D critical temperature, the adsorbed molecules become spread over the hydroxylated Cr_2O_3 in a less ordered fashion, leaving the nearest neighbor distance unchanged. Thus, we can identify the properties of 2D water adsorbed on a hydroxylated Cr_2O_3 surface, thermodynamically and structurally.

Our simulations suggest that water molecules are less structurally varied at temperatures below the 2D critical temperature, although there are discrepancies from the hexagonal net structure. This fact explains the experimental data obtained by dielectric and quasielastic neutron scattering (QENS) measurements. The dielectric relaxation activation energy of monolayer water is 48 kJmol^{-1} below the 2D critical temperature, which is very close to that of ice, and QENS measurements show that the rotational motion is significantly decreased above the 2D critical temperature.

4. Conclusions

The structure of monolayer water molecules on a hydroxylated Cr_2O_3 surface was studied using GCMC simulations employing the TIP3P potential for the water molecules. The experimental 2D phase diagram was described by the simulation, which gave the 2D critical temperature of $T = 319$ K. The structure of the monolayer of water below the 2D critical temperature is composed of a net of many hexagonal water molecules registered on the hexagonal structure of the hydroxylated surface.

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